



Europäisches Patentamt  
European Patent Office  
Office Européen des brevets



⑪ Publication number : 0 613 714 A2

⑫

## EUROPEAN PATENT APPLICATION

⑬ Application number : 94100256.0

⑮ Int. Cl.<sup>5</sup> : B01D 53/36

⑭ Date of filing : 10.01.94

⑯ Priority : 11.01.93 JP 2491/93  
20.08.93 JP 206664/93  
24.09.93 JP 238461/93

⑰ Date of publication of application :  
07.09.94 Bulletin 94/36

⑲ Designated Contracting States :  
DE FR GB

⑳ Applicant : TOYOTA JIDOSHA KABUSHIKI  
KAISHA  
1, Toyota-cho  
Toyota-shi  
Aichi-ken (JP)

㉑ Applicant : KABUSHIKI KAISHA TOYOTA  
CHUO KENKYUSHO  
41-1, Aza Yokomichi  
Oaza Nagakute  
Nagakute-cho  
Aichi-gun Aichi-ken, 480-11 (JP)

㉒ Applicant : CATALER INDUSTRIAL CO., LTD.  
7800, Chihama,  
Daito-cho  
Ogasa-gun, Shizuoka-ken (JP)

㉓ Inventor : Miyoshi, Naoto  
c/o Toyota Jidosha Kabushiki Kiasha,  
1, Toyota-cho  
Toyota-shi, Aichi-ken (JP)  
Inventor : Matsumoto, Shinichi  
c/o Toyota Jidosha Kabushiki Kiasha,  
1, Toyota-cho  
Toyota-shi, Aichi-ken (JP)  
Inventor : Tanizawa, Tsuneyuki  
c/o Toyota Jidosha Kabushiki Kiasha,  
1, Toyota-cho  
Toyota-shi, Aichi-ken (JP)  
Inventor : Iguchi, Satoshi  
c/o Toyota Jidosha Kabushiki Kiasha,  
1, Toyota-cho  
Toyota-shi, Aichi-ken (JP)  
Inventor : Tanaka, Toshiaki  
c/o Toyota Jidosha Kabushiki Kiasha,  
1, Toyota-cho  
Toyota-shi, Aichi-ken (JP)

Inventor : Takeshima, Shinichi  
c/o Toyota Jidosha Kabushiki Kiasha,  
1, Toyota-cho  
Toyota-shi, Aichi-ken (JP)  
Inventor : Kanazawa, Takaaki  
c/o Toyota Jidosha Kabushiki Kiasha,  
1, Toyota-cho  
Toyota-shi, Aichi-ken (JP)  
Inventor : Hayashi, Takahiro  
c/o Toyota Jidosha Kabushiki Kiasha,  
1, Toyota-cho  
Toyota-shi, Aichi-ken (JP)  
Inventor : Saiki, Motohisa, c/o K.K. Toyota  
Chuo Kenkyusho  
41-1, Aza Yokomichi,  
Oaza Nagakute,  
Nagakute-cho  
Aichi-gun, Aichi-ken (JP)  
Inventor : Dohmae, Kazuhiko, c/o K.K. Toyota  
Chuo Kenkyusho  
41-1, Aza Yokomichi,  
Oaza Nagakute,  
Nagakute-cho  
Aichi-gun, Aichi-ken (JP)  
Inventor : Yamazaki, Kiyoshi, c/o K.K. Toyota  
Chuo Kenkyusho  
41-1, Aza Yokomichi,  
Oaza Nagakute,  
Nagakute-cho  
Aichi-gun, Aichi-ken (JP)  
Inventor : Suzuki, Tadashi, c/o K.K. Toyota  
Chuo Kenkyusho  
41-1, Aza Yokomichi,  
Oaza Nagakute,  
Nagakute-cho  
Aichi-gun, Aichi-ken (JP)  
Inventor : Kasahaha, Koichi  
c/o Cataler Industrial Co., Ltd.,  
7800, Chihama  
Daito-cho, Ogasa-gun, Shizuoka-ken (JP)  
Inventor : Tateishi, Syuji  
c/o Cataler Industrial Co., Ltd.,  
7800, Chihama  
Daito-cho, Ogasa-gun, Shizuoka-ken (JP)

㉔ Representative : Bühlung, Gerhard, Dipl.-Chem.  
et al  
Patentanwaltsbüro  
Tiedtke-Bühlung-Kinne & Partner  
Bavarialring 4  
D-80336 München (DE)

㉕ Catalyst and process for purifying exhaust gases.

㉖ Disclosed are a catalyst and a process for purifying exhaust gases. The catalyst includes a porous support, Pt and/or Pd loaded on the porous support, and at least two ingredients loaded thereon and

EP 0 613 714 A2

EP 0 613 714 A2

capable of reacting with  $\text{NO}_x$  and  $\text{SO}_2$  contained in the exhaust gases to form nitrates and composite sulfates. Since the resulting composit sulfates are likely to decompose at low temperatures in the oxygen-lean atmospheres (i.e., in the fuel-rich atmospheres), the catalyst can absorb more  $\text{NO}_x$  thereon. As a result, the catalyst can purify more  $\text{NO}_x$ . Further, a second ingredient selected from the group consisting of transition elements can substitute for one of the two co-catalysts. Moreover, the catalyst is superb in the  $\text{NO}_x$  purifying performance even after being subjected to a harsh durability test. In the process, the catalyst is brought into contact with oxygen-rich exhaust gases, whose oxygen concentrations are the stoichiometric point or more required for oxidizing the components to be oxidized therein.

BACKGROUND OF THE INVENTIONField of the Invention

5 The present invention relates to a catalyst for purifying exhaust gases and a process for purifying exhaust gases. More particularly, it relates to the catalyst and the process which can efficiently purify nitrogen oxides (NO<sub>x</sub>) in the exhaust gases which contain oxygen in excessive amounts required for oxidizing carbon monoxide (CO) and hydrocarbons (HC) therein.

10 Description of Related Art

As catalysts for purifying automotive exhaust gases, there have been employed 3-way catalysts so far which oxidize CO and HC and reduces NO<sub>x</sub> simultaneously to purify the exhaust gases. For example, the 3-way catalysts have been known widely which comprise a heat resistant support formed of cordierite, a catalyst carrier layer formed of gamma-alumina and disposed on the support, and a noble metal selected from the group consisting of Pt, Pd and Rh and loaded on the catalyst carrier layer.

15 The purifying performance of the 3-way catalysts for purifying exhaust gases depends on the air-fuel ratio (A/F) of automotive engine. For instance, when the air-fuel ratio is large, i.e., when the fuel concentration is small (or on the fuel-lean side), the oxygen concentration is large. Accordingly, the oxidation reactions purifying CO and HC are active, but the reduction reactions purifying NO<sub>x</sub> are inactive. On the other hand, when the air-fuel ratio is small, i.e., when the fuel concentration is more (or on the fuel-rich side), the oxygen concentration is small. Accordingly, the oxidation reactions are inactive, but the reduction reactions are active.

20 Moreover, when driving automobiles, especially when driving automobiles in urban areas, the automobiles are accelerated and decelerated frequently. Consequently, the air-fuel ratio varies frequently in the range of from the values adjacent to the stoichiometric point (or the ideal air-fuel ratio) to the fuel-rich side. In order to satisfy the low fuel consumption requirement during the driving in urban areas, it is necessary to operate the automobiles on the fuel-lean side where the air-fuel mixture containing oxygen as excessive as possible is supplied to the engines. Hence, it has been desired to develop a catalyst which is capable of adequately purifying NO<sub>x</sub> on the fuel-lean side (i.e., in the oxygen-rich atmospheres).

25 30 Under the circumstances, as set forth in Japanese Unexamined Patent Publication (KOKAI) No. 5-168860, the applicants of the present invention disclosed a catalyst with rare-earth elements including La, and Pt loaded. With the catalyst, NO<sub>x</sub> is absorbed on the rare-earth elements during the fuel-lean side (i.e., in the oxygen-rich atmospheres) driving, and it is purified by reacting with the reducing gases such as HC and the like, when the automobiles are driven under the air-fuel ratios at the stoichiometric point or on the fuel-rich side (i.e., in the oxygen-lean atmospheres). Thus, the catalyst is superb in the purifying performance of NO<sub>x</sub> even on the fuel-lean side (i.e., in the oxygen-rich atmospheres). The catalyst is believed to provide the advantageous effect because the rare-earth elements are loaded on the support in a form of the simple oxides and the simple oxides of the rare-earth elements and they react with NO<sub>x</sub> so as to produce the nitrates thereof.

35 40 However, the exhaust gases usually contain SO<sub>2</sub> which are produced by burning sulfur (S) contained in the fuel. Further, the catalyst ingredient oxidizes SO<sub>2</sub> to SO<sub>3</sub> in the oxygen-rich atmospheres (i.e., on the fuel-lean side). Then, SO<sub>3</sub> reacts readily with water contained in the exhaust gases to produce sulfuric acid. The sulfate ions or the sulfite ions react with rare-earth elements to produce the sulfates or the sulfites incapable of absorbing NO<sub>x</sub>. Accordingly, the catalyst is not completely satisfactory in terms of the NO<sub>x</sub> purifying performance and the durability of the performance at elevated temperatures.

45 SUMMARY OF THE INVENTION

50 The present invention has been developed in view of the aforementioned circumstances. It is therefore an object of the present invention to efficiently purify NO<sub>x</sub> in exhaust gases containing oxygen in excessive amounts and improve the catalyst in terms of the durability of the NO<sub>x</sub> purifying performance at elevated temperatures.

55 In accordance with the present invention, a catalyst or a process comes to be able to carry out the above object, and they can simultaneously purify carbon monoxide, hydrocarbons and nitrogen oxides in exhaust gases in oxygen-rich atmospheres, thereby purifying the exhaust gases. It is one of the features of the present invention that novel and specific ingredients are loaded on the catalyst for purifying exhaust gases which is brought into contact with the exhaust gases containing oxygen in excessive amounts. Unless otherwise specified, the loading amounts of the catalyst ingredient or the following ingredients mean the amounts thereof loaded on a unit volume of a porous support and expressed in grams or moles with respect the unit volume

(e.g., 1 liter).

First of all, at least one catalyst ingredient selected from the group consisting of platinum (Pt) and palladium (Pd) is loaded on a catalyst according to the present. It is preferred to load rhodium (Rh) thereon in addition to Pt and Pd. The loading amount of the catalyst ingredient can preferably fall in a range of from 0.1 to 10 grams/liter when one of the catalyst ingredients are loaded thereon independently, and it can preferably fall in a range of from 0.1 to 10 grams/liter in total when they are combined and loaded thereon. The loading amount can further preferably fall in a range of 0.5 to 3.0 grams/liter.

In a first aspect of the present invention, a catalyst according to the present invention comprises, in addition to the above-described catalyst ingredients, at least two ingredients loaded thereon. The ingredients are selected from the group consisting of rare-earth elements including La, and they can preferably be lanthanides such as La, Pr, Nd and Sm. The loading amounts of the two ingredients can preferably fall in a range of from 0.05 to 2.0 moles/liter in total. When the ingredients are loaded in an amount of less than the lower limit, the durability of the  $\text{NO}_x$  purifying performance deteriorates at elevated temperatures. When the ingredients are loaded in an amount more than the upper limit, the advantageous effects resulting from the loading saturate, and the porous support diminishes the surface area. Hence, it is unpreferable to load the ingredients in such loading amounts deviating from the range.

In a second aspect of the present invention, a catalyst according to the present invention comprises, in addition to the above-described catalyst ingredients, at least one first ingredient loaded thereon, and at least one second ingredient loaded thereon. The first ingredient is selected from the group consisting of rare-earth elements including La. The second ingredient is selected from the group consisting of transition elements such as Fe, Ni, Co and Mn. The rare-earth elements including La can preferably be lanthanides such as La, Pr, Nd and Sm. The loading amount of the first ingredient (or the rare-earth element ingredient) can preferably fall in a range of from 0.05 to 1.0 mole/liter. The loading amount of the second ingredient (or the transition element ingredient) can preferably fall in a range of from 0.05 to 1.0 mole/liter. The loading amount of the first ingredient and the loading amount of the second ingredient can preferably fall in a range of from 0.1 to 2.0 moles/liter in total. When the first ingredient and the second ingredient are loaded in an amount of less than the lower limit, the durability of the  $\text{NO}_x$  purifying performance deteriorates at elevated temperatures. When the first ingredient and the second ingredient are loaded in an amount more than the upper limit, the advantageous effects resulting from the loading saturate, and the porous support diminishes the surface area. Hence, it is unpreferable to load the first ingredient and the second ingredient in such loading amounts deviating from the range.

In a third aspect of the present invention, a catalyst according to the present invention comprises, in addition to the above-described catalyst ingredients, at least two ingredients loaded thereon. The ingredients are selected from the group consisting of alkali metals, and they can preferably be K, Li, Na, Rb and Cs. The loading amounts of the two ingredients (or the two alkali metal ingredients) can preferably fall in a range of from 0.05 to 2.0 moles/liter in total. When the ingredients are loaded in an amount of less than the lower limit, the durability of the  $\text{NO}_x$  purifying performance deteriorates at elevated temperatures. When the ingredients are loaded in an amount more than the upper limit, the advantageous effects resulting from the loading saturate, and the porous support diminishes the surface area. Hence, it is unpreferable to load the ingredients in such loading amounts deviating from the range.

In a fourth aspect of the present invention, a catalyst according to the present invention comprises, in addition to the above-described catalyst ingredients, at least one first ingredient loaded thereon, and at least one second ingredient loaded thereon. The first ingredient is selected from the group consisting of alkali metals. The second ingredient is selected from the group consisting of rare-earth elements including La. The alkali metals can preferably be K, Li, Na, Rb and Cs. The rare-earth elements including La can preferably be lanthanides such as La, Pr, Nd and Sm. The loading amount of the first ingredient (or the alkali metal ingredient) can preferably fall in a range of from 0.05 to 1.0 mole/liter. The loading amount of the second ingredient (or the rare-earth element ingredient) can preferably fall in a range of from 0.05 to 1.0 mole/liter. The loading amount of the first ingredient and the loading amount of the second ingredient can preferably fall in a range of from 0.1 to 2.0 moles/liter in total. When the first ingredient and the second ingredient are loaded in an amount of less than the lower limit, the durability of the  $\text{NO}_x$  purifying performance deteriorates at elevated temperatures. When the first ingredient and the second ingredient are loaded in an amount more than the upper limit, the advantageous effects resulting from the loading saturate, and the porous support diminishes the surface area. Hence, it is unpreferable to load the first ingredient and the second ingredient in such loading amounts deviating from the range.

In a fifth aspect of the present invention, a catalyst according to the present invention comprises, in addition to the above-described catalyst ingredients, at least one first ingredient loaded thereon, and at least one second ingredient loaded thereon. The first ingredient is selected from the group consisting of alkali metals, and it can preferably be K, Li, Na, Rb and Cs. The second ingredient is selected from the group consisting of

transition elements, and it can preferably be Fe, Ni, Co and Mn. The loading amount of the first ingredient (or the alkali metal ingredient) can preferably fall in a range of from 0.05 to 1.0 mole/liter. The loading amount of the second ingredient (or the transition element ingredient) can preferably fall in a range of from 0.05 to 1.0 mole/liter. The loading amount of the first ingredient and the loading amount of the second ingredient can preferably fall in a range of from 0.1 to 2.0 moles/liter in total. When the first ingredient and the second ingredient are loaded in an amount of less than the lower limit, the durability of the  $\text{NO}_x$  purifying performance deteriorates at elevated temperatures. When the first ingredient and the second ingredient are loaded in an amount more than the upper limit, the advantageous effects resulting from the loading saturate, and the porous support diminishes the surface area. Hence, it is unpreferable to load the first ingredient and the second ingredient in such loading amounts deviating from the range.

In a sixth aspect of the present invention, a catalyst according to the present invention comprises, in addition to the above-described catalyst ingredients, at least two ingredients loaded thereon. The two ingredients are selected from the group consisting of alkaline-earth metals, and they can preferably be Mg, Ca, Ba and Sr. The loading amount of each of the two ingredients (or the two alkaline-earth metal ingredients) can preferably fall in a range of from 0.05 to 1.0 mole/liter, and the loading amounts of the two ingredients can preferably fall in a range of from 0.1 to 2.0 moles/liter in total. When the ingredients are loaded in an amount of less than the lower limit, the durability of the  $\text{NO}_x$  purifying performance deteriorates at elevated temperatures. When the ingredients are loaded in an amount more than the upper limit, the advantageous effects resulting from the loading saturate, and the porous support diminishes the surface area. Hence, it is unpreferable to load the ingredients in such loading amounts deviating from the range.

In a seventh aspect of the present invention, a catalyst according to the present invention comprises, in addition to the above-described catalyst ingredients, at least one first ingredient loaded thereon, and at least one second ingredient loaded thereon. The first ingredient is selected from the group consisting of alkaline-earth metals, and it can preferably be Mg, Ca, Ba and Sr. The second ingredient is selected from the group consisting of rare-earth elements including La, and it can preferably be one of lanthanides such as La, Pr, Nd and Sm. The loading amount of the first ingredient (or the alkaline-earth metal ingredient) can preferably fall in a range of from 0.05 to 1.0 mole/liter. The loading amount of the second ingredient (or the rare-earth element ingredient) can preferably fall in a range of from 0.05 to 1.0 mole/liter. The loading amount of the first ingredient and the loading amount of the second ingredient can preferably fall in a range of from 0.1 to 2.0 moles/liter in total. When the first ingredient and the second ingredient are loaded in an amount of less than the lower limit, the durability of the  $\text{NO}_x$  purifying performance deteriorates at elevated temperatures. When the first ingredient and the second ingredient are loaded in an amount more than the upper limit, the advantageous effects resulting from the loading saturate, and the porous support diminishes the surface area. Hence, it is unpreferable to load the first ingredient and the second ingredient in such loading amounts deviating from the range.

In an eighth aspect of the present invention, a catalyst according to the present invention comprises, in addition to the above-described catalyst ingredients, a plurality of ingredients compositely loaded thereon. The ingredients are Ba, Li, La, Ce and Zr. These five ingredients can be compounded in any composition unlimitedly. However, when the porous support is formed of alumina, it is preferred that Ba is compounded in an amount of from 8 to 45 mole % to 100 mole % of alumina, Li is compounded in an amount of from 4 to 18 mole % thereto, La is compounded in an amount of from 4 to 12 mole % thereto, Ce is compounded in an amount of from 17 to 45 mole % thereto, and Zr is compounded in an amount of from 4 to 9 mole % thereto.

As to a material for constituting the porous support, it can, for example, be alumina, zeolite, zirconia, silica alumina, silica, or the like. These materials can be formed into the porous support, or they can be coated on a honeycomb support formed of cordierite, heat resistant metal, or the like.

In accordance with a process of the present invention for purifying exhaust gases, either one of the eight present catalysts is brought into contact with oxygen-rich exhaust gases, whose oxygen concentrations are the stoichiometric point or more required for oxidizing the components to be oxidized therein, thereby purifying the exhaust gases.

In the first aspect of the present invention, the present catalyst comprises at least two ingredients selected from the group consisting of rare-earth elements including La and loaded compositely on the porous support. The two ingredients retrieve  $\text{SO}_2$  contained in the exhaust gases into the present catalyst in a form of composite sulfates.

In the second aspect of the present invention, the present catalyst comprises at least one first ingredient selected from the group consisting of rare-earth elements including La, and at least one second ingredient selected from the group consisting of Fe, Ni, Co and Mn. The first and second ingredients are loaded compositely on the porous support, and they retrieve  $\text{SO}_2$  contained in the exhaust gases into the present catalyst in a form of composite sulfates.

In the third aspect of the present invention, the present catalyst comprises at least two ingredients selected

form the group consisting of alkali metals and loaded compositely on the porous support. The two ingredients retrieve SO<sub>2</sub> contained in the exhaust gases into the present catalyst in a form of composite sulfates.

In the fourth aspect of the present invention, the present catalyst comprises at least one first ingredient selected from the group consisting of alkali metals, and at least one second ingredient selected from the group consisting of rare-earth elements including La. The first and second ingredients are loaded compositely on the porous support, and they retrieve SO<sub>2</sub> contained in the exhaust gases into the present catalyst in a form of composite sulfates.

In the fifth aspect of the present invention, the present catalyst comprises at least one first ingredient selected from the group consisting of alkali metals, and at least one second ingredient selected from the group consisting of Fe, Ni, Co, and Mn. The first and second ingredients are loaded compositely on the porous support, and they retrieve SO<sub>2</sub> contained in the exhaust gases into the present catalyst in a form of composite sulfates.

In the sixth aspect of the present invention, the present catalyst comprises at least two ingredients selected from the group consisting of alkaline-earth metals and loaded compositely on the porous support. The two ingredients retrieve SO<sub>2</sub> contained in the exhaust gases into the present catalyst in a form of composite sulfates.

In the seventh aspect of the present invention, the present catalyst comprises at least one first ingredient selected from the group consisting of alkaline-earth metals, and at least one second ingredient selected from the group consisting of rare-earth elements including La. The first and second ingredients are loaded compositely on the porous support, and they retrieve SO<sub>2</sub> contained in the exhaust gases into the present catalyst in a form of composite sulfates.

In the eighth aspect of the present invention, the present catalyst comprises the five ingredients, e.g., Ba, Li, La, Ce and Zr, and loaded compositely on the porous support. The five ingredients retrieve SO<sub>2</sub> contained in the exhaust gases into the present catalyst in a form of composite sulfates.

In the process for purifying exhaust gases according to the present invention, either one of the eight present catalysts is brought into contact with the oxygen-rich exhaust gases. Hence, SO<sub>2</sub> contained in the exhaust gases is retrieved by the action of the ingredients into the present catalysts in a form of composite sulfates.

The resulting composite sulfates are more likely to decompose at low temperatures in the atmospheres ranging from the stoichiometric atmosphere to the fuel-rich atmospheres (i.e., in the oxygen-lean atmospheres) than the simple sulfates resulting from the independent ingredients. As a result, the rare-earth element ingredients including La, the alkali metal ingredients and the alkaline-earth metal ingredients can reproduce their NO<sub>x</sub> storage abilities because the composite sulfates are likely to decompose and release SO<sub>2</sub>.

Thus, in the fuel-lean atmospheres (i.e., in the oxygen-rich atmospheres), NO<sub>x</sub> is absorbed or stored in the present catalyst for purifying exhaust gases. Then, in atmospheres ranging from the stoichiometric atmosphere to the fuel-rich atmospheres (i.e., in the oxygen-lean atmospheres), NO<sub>x</sub> is reacted with CO and HC contained in the exhaust gases, and it is reduced to N<sub>2</sub>. Namely, in the atmospheres ranging from stoichiometric atmosphere to the fuel-rich atmospheres (i.e., in the oxygen-lean atmospheres), NO<sub>x</sub> is reduced and purified, and at the same time CO and HC are oxidized and purified as well.

With the above-described mechanism, it is believed that the present catalyst for purifying exhaust gases can maintain the NO<sub>x</sub> absorbing ability for a long period of time, and accordingly it can keep the catalyst activity high. In addition, when at least two of the rare-earth element ingredients, the alkali metal ingredients and the alkaline-earth metal ingredients are loaded compositely, they come to have smaller particle diameters, and they hardly grow to the crystalline sulfates because the composite sulfates are likely to decompose and release SO<sub>2</sub>. As a result, they can be kept to be highly dispersed for a long period of time, they can produce large surface areas capable of contacting NO<sub>x</sub>, and they can be disposed close to Pt and/or Pd so as to facilitate the catalyst reaction. Hence, the composite loading is believed to be one of the reasons why the present catalyst can keep the high catalyst activity even after it is subjected to a harsh durability test.

In particular, in the eighth aspect of the present invention, it is still under investigation how the five ingredients operate compositely or cooperatively so as to improve the durability of the present catalyst. However, the durability is believed to be enhanced, because Ba is a major component absorbing NO<sub>x</sub> and SO<sub>2</sub>, and because the other four ingredients, e.g., Li, La, Ce and Zr, enable to readily decompose the composite sulfates resulting from the compounding of Ba and SO<sub>2</sub> or they act on the porous support, for instance, on the porous support formed of alumina, so as to prevent alumina from reacting with Ba.

As having been described so far, in accordance with the present catalyst for purifying exhaust gases or the present process therefor, superb NO<sub>x</sub> purifying performance can be maintained even after a durability test is carried out, and NO<sub>x</sub> can be purified efficiently even in the atmospheres on the fuel-lean side where the exhaust gases contain oxygen in excessive amounts.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Having generally described the present invention, a further understanding can be obtained by reference to the specific preferred embodiments which are provided herein for purposes of illustration only and are not intended to limit the scope of the appended claims. Unless otherwise specified, a term, "parts," hereinafter means "parts by weight."

First Preferred Embodiments

10 100 parts of an alumina powder, 70 parts of alumina sol containing alumina in an amount of 10% by weight, 15 parts of an aqueous aluminum nitrate solution containing aluminum nitrate in an amount of 40% by weight, and 30 parts of water were mixed, thereby preparing a slurry for coating.

15 Then, a plurality of honeycomb supports formed of cordierite were immersed into the slurry, and thereafter each of them was blown to blow away the slurry in excess. After drying, each of the supports was burned at 600 °C for 1 hour, thereby forming an alumina coating layer thereon. The alumina coating layer was thus coated on the support in an amount of 120 grams with respect to 1 liter of the support.

20 Each of the honeycomb supports with the alumina coating layer formed thereon was immersed into an aqueous platinum dinitrodiammime solution or an aqueous palladium nitrate solution, and thereafter it was blown to blow away the water droplets in excess. After the blowing, each of the supports was dried at 250 °C for 3 hours, thereby loading Pt or Pd thereon. The loading amounts of Pt or Pd are set forth in Table 1 below.

25 Finally, each of the honeycomb supports with Pt or Pd loaded was immersed into a mixed aqueous solution which contains nitrates of rare-earth elements including La in predetermined concentrations. The term, "rare-earth elements," hereinafter means "rare-earth elements including La." The rare-earth elements employed were La, Pr, Nd and Sm. Each of the mixed aqueous solutions was prepared by mixing the nitrates of rare-earth elements with water so as to load the rare-earth element ingredients in loading amounts set forth in Table 1 below. Each of the supports was then blown to blow away the water droplets in excess. After drying, each of the supports was burned at 600 °C for 1 hour, thereby completing each of the present catalysts designated at No. 1 through No. 9 in Table 1.

30 Second Preferred Embodiments

35 A plurality of honeycomb supports with Pt loaded were prepared in the same manner as described in the "First Preferred Embodiments" section. Then, each of the supports was immersed into a mixed aqueous solution which contains not only a nitrate of rare-earth elements but also a nitrate of transition elements in predetermined concentrations. Each of the mixed aqueous solutions was prepared by mixing the nitrate of rare-earth elements and the nitrate of transition elements with water so as to load the rare-earth element ingredient and the transition element ingredient in loading amounts set forth in Table 1 below. The transition elements employed were Fe, Ni, Co and Mn. Each of the supports was then blown to blow away the water droplets in excess. After drying, each of the supports was burned at 600 °C for 1 hour, thereby completing each of the 40 present catalysts designated at No. 10 through No. 21 in Table 1.

First Comparative Examples

45 First Comparative Examples, e.g., comparative catalysts designated at No. 22 through No. 29 in Table 1 below, were prepared in the same manner as described in the "First Preferred Embodiments" section except that each of the honeycomb supports with Pt or Pd loaded was immersed into an aqueous solution which contains one and only nitrate of rare-earth elements, thereby loading one and only rare-earth element ingredient thereon.

TABLE 1

Loading Amount, Loading Amount, Initial  
Catalyst Ingredient Rare-earth Element Conversion  
(gram/liter) Ingredient (mole/liter) Transition Element  
after Durability Test (%)

	Pt	Pd	La	Pr	Nd	Sm	Fe	Ni	Co	Mn	NOx	CO	HC	CO		
1st	No. 1	2.0	-	0.15	0.15	-	-	-	-	-	92	98	100	52	98	100
Pref.	No. 2	2.0	-	0.15	-	0.15	-	-	-	-	93	98	100	55	97	99
Embodi-	No. 3	2.0	-	0.15	-	0.15	-	-	-	-	92	98	100	53	98	100
ments	No. 4	2.0	-	-	0.15	0.15	-	-	-	-	90	98	100	50	97	99
No. 5	2.0	-	-	0.15	-	0.15	-	-	-	-	90	97	100	53	98	100
No. 6	2.0	-	-	0.15	0.15	0.15	-	-	-	-	91	98	100	53	98	100
No. 7	-	3.0	-	0.15	0.15	-	-	-	-	-	92	98	100	48	96	100
No. 8	-	3.0	-	0.15	-	0.15	-	-	-	-	93	98	100	45	95	99
No. 9	-	3.0	-	0.15	-	0.15	-	-	-	-	92	98	100	41	95	100
2nd	No. 10	2.0	-	0.30	-	-	0.10	-	-	-	90	98	100	54	97	99
Pref.	No. 11	2.0	-	0.30	-	-	0.10	-	-	-	90	97	100	53	97	99
Embodi-	No. 12	2.0	-	0.30	-	-	-	0.10	-	-	89	99	100	50	96	100
ments	No. 13	2.0	-	0.30	-	-	-	-	0.10	-	88	97	100	51	96	99
No. 14	2.0	-	-	0.30	-	-	0.10	-	-	-	89	97	100	49	95	99
No. 15	2.0	-	-	0.30	-	0.10	-	-	-	-	88	98	100	50	96	99
No. 16	2.0	-	-	0.30	-	-	0.10	-	-	-	86	95	100	51	95	99
No. 17	2.0	-	-	-	0.30	-	-	0.10	-	-	86	96	100	48	96	100
No. 18	2.0	-	-	-	0.30	-	-	0.10	-	-	87	98	100	48	95	100
No. 19	2.0	-	-	-	0.30	-	0.10	-	-	-	88	97	100	50	96	100
No. 20	2.0	-	-	-	0.30	-	0.10	-	-	-	85	97	100	33	95	99
No. 21	2.0	-	-	-	0.30	-	0.10	-	-	-	86	97	100	34	95	99
1st	No. 22	2.0	-	0.30	-	-	-	-	-	-	91	97	100	34	98	100
Comp.	No. 23	2.0	-	-	0.30	-	-	-	-	-	89	99	100	32	98	99
Ex.	No. 24	2.0	-	-	-	0.30	-	-	-	-	88	98	100	30	97	100
	No. 25	2.0	-	-	-	-	0.30	-	-	-	88	98	100	30	98	99
	No. 26	-	3.0	-	0.30	-	-	-	-	-	69	97	100	44	95	99
	No. 27	-	3.0	-	0.30	-	-	-	-	-	67	97	100	28	93	100
	No. 28	-	3.0	-	-	0.30	-	-	-	-	65	99	100	26	94	100
	No. 29	-	3.0	-	-	-	0.30	-	-	-	65	97	100	26	93	100

Examination for Purifying Performance

5 Each of the present catalysts and the comparative catalysts was disposed in an exhaust line of an actual vehicle equipped with a lean burn engine. The lean burn engine had a displacement of 1.6 liters. The vehicle was driven in the urban area running mode, for instance, it was alternately driven in the 10-mode for a certain period of time and then in the 15-mode for another certain period of time, thereby examining the present and comparative catalysts for the conversion of CO, HC and NO<sub>x</sub>. The results of the evaluation were summarized in the columns designated at "Initial Conversion" in Table 1.

10 After the aforementioned evaluation, each of the present catalysts and the comparative catalysts was subjected to a bench test on durability which utilized the same type of engine as above. Namely, each of them was disposed in an exhaust line of the engine, and then the engine was run for 100 hours while adjusting the temperature of the exhaust gas introduced into them at 650 °C. After this bench test was over, each of them was again disposed in the exhaust line of the actual vehicle. The vehicle was driven in the same manner as described above, thereby examining the present and comparative catalysts for the conversion of CO, HC and NO<sub>x</sub>. The results of the evaluation were summarized in the columns designated at "Conversion after Durability Test" in Table 1.

Evaluation

20 It is appreciated from Table 1 that the present catalysts with two rare-earth element ingredients loaded, the present catalysts with a rare-earth element ingredient and a transition element ingredient loaded were improved in terms of the NO<sub>x</sub> conversion after the durability test over the comparative catalysts with one and only rare-earth element ingredient loaded.

Third Preferred Embodiments

A plurality of honeycomb supports were prepared by coating them with the alumina coating layer in the same manner as described in the "First Preferred Embodiments" section.

30 Each of the honeycomb supports with the alumina coating layer formed thereon was immersed into an aqueous platinum dinitrodiammine solution or an aqueous palladium nitrate solution, and thereafter it was blown to blow away the water droplets in excess. After the blowing, each of the supports was dried at 250 °C for 3 hours, thereby loading Pt or Pd thereon. The loading amounts of Pt or Pd are set forth in Table 2 below.

35 Then, each of the supports with Pt or Pd loaded was immersed into a mixed aqueous solution which contains nitrates of alkali metals in predetermined concentrations. Each of the mixed aqueous solutions was prepared by mixing the nitrates of alkali metals with water so as to load the alkali metal ingredients in loading amounts set forth in Table 2 below. The alkali metals employed were Li, Na, K, Rb and Cs. Each of the supports was then blown to blow away the water droplets in excess. After drying, each of the supports was burned at 600 °C for 1 hour, thereby completing each of the present catalysts designated at No. 30 through No. 41 in Table 2.

Fourth Preferred Embodiments

40 A plurality of honeycomb supports with Pt loaded were prepared in the same manner as described in the "First Preferred Embodiments" section. Then, each of the supports was immersed into a mixed aqueous solution which contains not only a nitrate of alkali metals but also a nitrate of rare-earth elements in predetermined concentrations. Each of the mixed aqueous solutions was prepared by mixing the nitrate of alkali metals and the nitrate of rare-earth elements with water so as to load the alkali metal ingredient and the rare-earth element ingredient in loading amounts set forth in Table 3 below. Each of the supports was then blown to blow away the water droplets in excess. After drying, each of the supports was burned at 600 °C for 1 hour, thereby completing each of the present catalysts designated at No. 51 through No. 64 in Table 3.

Fifth Preferred Embodiments

45 A plurality of honeycomb supports with Pt loaded were prepared in the same manner as described in the "First Preferred Embodiments" section. Then, each of the supports was immersed into a mixed aqueous solution which contains not only a nitrate of alkali metals but also a nitrate of transition elements in predetermined concentrations. Each of the mixed aqueous solutions was prepared by mixing the nitrate of alkali metals and the nitrate of transition elements with water so as to load the alkali metal ingredient and the transition element

ingredient in loading amounts set forth in Table 4 below. Each of the supports was then blown to blow away the water droplets in excess. After drying, each of the supports was burned at 600 °C for 1 hour, thereby completing each of the present catalysts designated at No. 65 through No. 76 in Table 4.

5

10

15

20

25

30

35

40

45

50

55

TABLE 2

Catalyst Ingredient (gram/liter)	Loading Amount, Alkali Metal Ingredient (mole/liter)	Initial Conversion (%)						Conversion after Durability Test (%)		
		Pt	Pd	Li	Na	Rb	Ps	NOx	CO	HC
3rd Pref.	No. 30 2.0	-	-	0.10	0.30	-	-	89	94	100
Embodi- ments	No. 31 2.0	-	-	0.10	-	0.30	-	91	92	100
	No. 32 2.0	-	-	0.10	-	-	0.30	75	92	100
	No. 33 2.0	-	-	0.10	-	-	-	77	90	100
	No. 34 2.0	-	-	-	0.10	0.30	-	-	48	92
	No. 35 2.0	-	-	-	0.30	0.10	-	-	95	100
	No. 36 2.0	-	-	-	-	0.30	-	92	96	100
	No. 37 2.0	-	-	-	-	0.30	-	90	90	92
	No. 38 2.0	-	-	-	-	0.10	-	0.10	91	93
	No. 39 -	-	-	0.30	-	-	-	-	92	92
	No. 40 -	-	-	0.30	-	0.10	-	-	97	100
	No. 41 -	-	-	-	-	0.30	0.10	-	42	93
				-	-	-	-	77	95	98
				-	-	-	-	96	100	98
				-	-	-	-	46	94	97
2nd Comp. Ex.	No. 42 2.0	-	-	0.10	-	-	-	-	98	100
	No. 43 2.0	-	-	0.30	-	-	-	-	72	97
	No. 44 2.0	-	-	-	0.30	-	-	-	88	94
	No. 45 2.0	-	-	-	-	0.30	-	-	70	90
	No. 46 2.0	-	-	-	-	-	0.30	-	64	93
	No. 47 2.0	-	-	-	-	-	-	70	90	100
	No. 48 -	-	-	0.30	-	-	-	-	99	91
	No. 49 -	-	-	0.30	-	-	-	-	94	98
	No. 50 -	-	-	-	0.30	-	-	-	74	95
				-	-	-	-	-	27	90
				-	-	-	-	-	98	98
				-	-	-	-	-	32	88
				-	-	-	-	-	97	97

5  
10  
15  
20  
25  
30  
35  
40  
45  
50  
55

EP 0 613 714 A2

	Pt	Pd	Loading Amount, Catalyst Ingredient (gram/liter)			Loading Amount, Alkali Metal Ingredient (mole/liter)			Initial Conversion (%)			Conversion after Durability Test (%)					
			Li	Na	K	Rb	Cs	La	Pr	Nd	Sm	NO <sub>x</sub>	HC	CO	NO <sub>x</sub>	HC	CO
4th	No. 51	2.0	-	0.30	-	-	-	0.10	-	-	-	85	95	100	47	97	99
Ref.	No. 52	2.0	-	0.10	-	-	-	0.30	-	-	-	90	95	100	54	98	100
Embodi- ments	No. 53	2.0	-	0.30	-	-	-	-	-	-	-	83	93	100	47	96	99
	No. 54	2.0	-	0.10	-	-	-	-	-	-	-	91	96	100	57	96	100
	No. 55	2.0	-	0.30	-	-	-	0.10	-	-	-	88	92	100	56	96	100
	No. 56	2.0	-	0.30	-	-	-	-	0.10	-	-	87	93	100	53	94	100
	No. 57	2.0	-	0.30	-	-	-	-	0.10	-	-	90	94	100	54	96	100
	No. 58	2.0	-	0.30	-	-	-	-	-	-	-	91	92	100	53	95	100
	No. 59	2.0	-	-	-	0.30	-	-	0.10	-	-	92	90	100	58	94	99
	No. 60	2.0	-	-	-	0.30	-	-	0.10	-	-	91	94	100	59	96	99
	No. 61	2.0	-	-	-	0.30	-	-	-	0.10	-	92	91	100	57	95	99
	No. 62	2.0	-	-	-	0.30	-	-	-	0.10	-	90	92	100	56	95	99
	No. 63	2.0	-	-	-	-	0.30	0.10	-	-	90	93	100	51	96	98	
	No. 64	2.0	-	-	-	-	0.30	-	0.10	-	90	94	100	51	95	98	
2nd	No. 42	2.0	-	0.10	-	-	-	-	-	-	-	63	98	100	30	95	99
Comp.	No. 43	2.0	-	0.30	-	-	-	-	-	-	-	72	97	100	34	94	99
Ex.	No. 44	2.0	-	0.30	-	-	-	-	-	-	-	88	94	100	37	92	100
	No. 45	2.0	-	-	0.30	-	-	-	-	-	-	88	93	100	38	93	99
	No. 46	2.0	-	-	-	0.30	-	-	-	-	-	70	90	100	31	90	100
	No. 47	2.0	-	-	-	0.30	-	-	-	-	-	70	90	100	30	91	100
	No. 48	-	3.0	-	0.30	-	-	-	-	-	-	64	93	99	27	90	99
	No. 49	-	3.0	-	0.30	-	-	-	-	-	-	73	94	98	30	88	98
	No. 50	-	3.0	-	-	0.30	-	-	-	-	-	74	95	98	32	88	97

Pt	Pd	Loading Amount, Catalyst Ingredient (gram/liter)			Loading Amount, Alkali Metal Ingredient (mole/liter)			Initial Conversion (%)			Conversion after Durability Test (%)				
		Li	Na	K	Rb	Cs	Fe	Ni	Co	Mn	NOx	HC	CO	HC	CO
5th Pref.	No. 65 No. 66	2.0 2.0	- -	0.30 0.30	- -	- -	0.10 0.10	- -	- -	72 70	96 97	100 100	45 47	95 98	99 100
Embodi- ments		No. 67 No. 68	2.0 2.0	- -	0.30 0.30	- -	0.10 0.10	- -	- -	86 87	97 98	100 100	51 53	96 96	99 100
No. 69 No. 70		2.0 2.0	- -	0.30 0.30	- -	- -	0.10 0.10	- -	- -	85 87	96 96	100 100	52 53	97 96	100 100
No. 71 No. 72		2.0 2.0	- -	0.30 0.30	- -	0.10 0.10	- -	- -	- -	87 89	99 99	100 100	52 56	96 95	100 100
No. 73 No. 74		2.0 2.0	- -	0.30 0.30	- -	- -	0.10 0.10	- -	- -	89 88	98 98	100 100	57 57	94 96	99 99
No. 75 No. 76		2.0 2.0	- -	0.30 0.30	- -	0.10 0.10	- -	- -	- -	73 75	97 97	100 100	49 48	98 95	99 99
2nd Comp.		No. 42 No. 43	2.0 2.0	0.10 0.30	- -	- -	- -	- -	- -	63 72	98 97	100 100	30 34	95 94	99 99
Ex.		No. 44 No. 45	2.0 2.0	- -	0.30 0.30	- -	- -	- -	- -	88 88	94 93	100 100	37 38	92 93	100 99
No. 46 No. 47		2.0 2.0	- -	- -	0.30 0.30	- -	- -	- -	- -	70 70	90 90	100 100	31 30	90 91	100 100
No. 48 No. 49		- -	3.0 3.0	0.30 0.30	- -	0.30 0.30	- -	- -	- -	64 73	93 94	99 98	27 30	90 68	99 98
No. 50		- -	3.0 3.0	- -	0.30 0.30	- -	- -	- -	- -	74 74	95 98	97 98	32 32	88 88	97 97

Second Comparative Examples

5 Second Comparative Examples, e.g., comparative catalysts designated at No. 42 through No. 50 in Tables 2, 3 and 4, were prepared in the same manner as described in the "Third, Fourth and Fifth Preferred Embodiments" sections except that each of the honeycomb supports with Pt or Pd loaded was immersed into an aqueous solution which contains one and only nitrate of alkali metals, thereby loading one and only alkali metal ingredient thereon.

Examination for Purifying Performance

10 Each of the present catalysts and the comparative catalysts was disposed in an exhaust line of an actual vehicle equipped with a lean burn engine. The lean burn engine had a displacement of 1.6 liters. The vehicle was driven in the urban area running mode, for instance, it was alternately driven in the 10-mode for a certain period of time and then in the 15-mode for another certain period of time, thereby examining the present and comparative catalysts for the conversion of CO, HC and NO<sub>x</sub>. The results of the evaluation were summarized in the columns designated at "Initial Conversion" in Tables 2, 3 and 4.

15 After the aforementioned evaluation, each of the present catalysts and the comparative catalysts was subjected to a bench test on durability which utilized the same type of engine as above. Namely, each of them was disposed in an exhaust line of the engine, and then the engine was run for 100 hours while adjusting the 20 temperature of the exhaust gas introduced into them at 650 °C. After this bench test was over, each of them was again disposed in the exhaust line of the actual vehicle. The vehicle was driven in the same manner as described above, thereby examining the present and comparative catalysts for the conversion of CO, HC and NO<sub>x</sub>. The results of the evaluation were summarized in the columns designated at "Conversion after Durability 25 Test" in Tables 2,3 and 4.

Evaluation

30 It is appreciated from Tables 2, 3 and 4 that the present catalysts with two alkali metal ingredients loaded, the present catalysts with an alkali metal ingredient and a rare-earth element ingredient loaded, and the present catalyst with an alkali metal ingredient and a transition element ingredient loaded were improved in terms of the NO<sub>x</sub> conversion after the durability test over the comparative catalysts with one and only alkali metal ingredient loaded.

Sixth Preferred Embodiments

35 A plurality of honeycomb supports were prepared by coating them with the alumina coating layer in the same manner as described in the "First Preferred Embodiments" section.

40 Each of the honeycomb supports with the alumina coating layer formed thereon was immersed into an aqueous platinum dinitrodiimine solution and/or an aqueous palladium nitrate solution, and thereafter it was blown to blow away the water droplets in excess. After the blowing, each of the supports was dried at 250 °C for 3 hours, thereby loading Pt and/or Pd thereon. The loading amounts of Pt and/or Pd are set forth in Table 5 below.

45 Then, each of the supports with Pt and/or Pd loaded was immersed into a mixed aqueous solution which contains two nitrates of alkaline-earth metals in predetermined concentrations. Each of the mixed aqueous solutions was prepared by mixing the two nitrates of alkali metals with water so as to load the two alkaline-earth metals in loading amounts set forth in Table 5 below. The alkaline-earth metals employed were Ba, Mg, Ca and Sr, and they are combined and loaded. Each of the supports was then blown to blow away the water droplets in excess. After drying, each of the supports was burned at 600 °C for 1 hour, thereby completing each of the present catalysts designated at No. 77 through No. 90 in Table 5.

50

55

Catalyst Ingredient (gram/liter)	Loading Amount, Alkaline-earth Metal Ingredient (mole/liter)						Initial Conversion (%)			Conversion after Durability Test (%)		
	Pt	Pd	Ba	Mg	Ca	Sr	NOx	HC	CO	NOx	HC	CO
6th Ref. Embodi- ments	No. 77 No. 78 No. 79 No. 80 No. 81 No. 82 No. 83 No. 84 No. 85 No. 86 No. 87 No. 88 No. 89 No. 90	2.0 2.0 2.0 2.0 2.0 2.0 2.0 2.0 2.0 2.0 1.0 1.0 2.0 3.0 3.0	- - - - - - - - - - - - - - -	0.3 0.3 0.5 0.3 0.5 0.3 0.3 0.5 0.1 0.2 0.1 0.2 0.1 0.2 0.2	0.1 0.2 0.2 0.1 0.1 0.3 0.3 0.5 0.1 0.2 0.1 0.2 0.1 0.2 0.2	- - - - - - - - - - - - - - -	92 93 92 93 92 96 95 92 93 92 96 95 96 95 94	98 98 98 94 93 96 95 96 93 96 96 95 96 95 94	100 100 100 100 100 100 100 100 100 100 100 100 100 100 100	66 65 66 54 55 58 57 59 57 59 59 51 52 49 50	94 93 93 88 89 92 90 91 90 91 91 99 99 92 93	99 100 99 100 99 99 100 100 99 100 100 99 100 100 99
3rd Comp. Ex.	No. 91 No. 92 No. 93 No. 94	2.0 2.0 3.0 1.0	- - - 2.0	0.3 0.3 0.3 2.0	- - - - - - - - - - - - - - -	- - - - - - - - - - - - - - -	92 69 78 0.3	94 97 96 0.3	100 100 100 84	50 38 40 96	88 91 88 100	

### Third Comparative Examples

Third Comparative Examples, e.g., comparative catalysts designated at No. 91 through No. 94 in Table 5, were prepared in the same manner as described in the "Sixth Preferred Embodiments" section except that each of the honeycomb supports with Pt and/or Pd loaded was immersed into an aqueous solution which contains one and only nitrate of alkaline-earth metals, thereby loading one and only alkaline-earth metal ingredient thereon.

Examination for Purifying Performance

5 Each of the present catalysts and the comparative catalysts was disposed in an exhaust line of an actual vehicle equipped with a lean burn engine. The lean burn engine had a displacement of 1.6 liters. The vehicle was driven in the urban area running mode, for instance, it was alternately driven in the 10-mode for a certain period of time and then in the 15-mode for another certain period of time, thereby examining the present and comparative catalysts for the conversion of CO, HC and NO<sub>x</sub>. The results of the evaluation were summarized in the columns designated at "Initial Conversion" in Table 5.

10 After the aforementioned evaluation, each of the present catalysts and the comparative catalysts was subjected to a bench test on durability which utilized the same type of engine as above. Namely, each of them was disposed in an exhaust line of the engine, and then the engine was run for 100 hours while adjusting the temperature of the exhaust gas introduced into them at 650 °C. After this bench test was over, each of them was again disposed in the exhaust line of the actual vehicle. The vehicle was driven in the same manner as described above, thereby examining the present and comparative catalysts for the conversion of CO, HC and NO<sub>x</sub>. The results of the evaluation were summarized in the columns designated at "Conversion after Durability Test" in Table 5.

Evaluation

20 It is appreciated from Table 5 that the present catalysts with two alkaline-earth metal ingredients loaded were improved in terms of the NO<sub>x</sub> conversion after the durability test over the comparative catalysts with one and only alkaline-earth metal ingredient loaded. Among the present catalyst, it is apparent that the present catalysts No. 77 through No. 79 on which the combination of Ba and Mg were loaded exhibited distinguished advantageous effects over the other present catalysts.

25 Seventh Preferred Embodiments

30 A plurality of honeycomb supports with Pt and/or Pd loaded were prepared in the same manner as described in the "First Preferred Embodiments" section. Then, each of the supports was immersed into a mixed aqueous solution which contains not only a nitrate of alkaline-earth metals but also a nitrate of rare-earth elements in predetermined concentrations. Each of the mixed aqueous solutions was prepared by mixing the nitrate of alkaline-earth metals and the nitrate of rare-earth elements with water so as to load the alkaline-earth metal ingredient and the rare-earth element ingredient in loading amounts set forth in Table 6 below. Each of the supports was then blown to blow away the water droplets in excess. After drying, each of the supports was burned at 600 °C for 1 hour, thereby completing each of the present catalysts designated at No. 95 through No. 111 in Table 6.

Fourth Comparative Examples

40 Fourth Comparative Examples, e.g., comparative catalysts designated at No. 112 through No. 115 in Table 6 below, were prepared in the same manner as described in the "Seventh Preferred Embodiments" section except that each of the honeycomb supports with Pt or Pd loaded was immersed into an aqueous solution which contains one and only nitrate of alkaline-earth metals, thereby loading one and only alkaline-earth metal ingredient thereon.

45

50

55

5  
10  
15  
20  
25  
30  
35  
40  
45  
50  
55

EP 0 613 714 A2

	Pt	Pd	Ba	Ca	Sr	Mg	La	Ce	Nd	Sm	Nox	HC	CO	NOx	HC	CO	Conversion	
																	7th	Pre.
7th	No. 95	2.0	-	0.3	-	-	0.1	-	-	-	91	100	63	97	100			
Pre.	No. 96	2.0	-	0.3	-	-	0.3	-	-	-	89	100	65	99	100			
Embody- ments	No. 97	2.0	-	0.3	-	-	0.1	-	-	-	88	98	62	96	99			
No.	98	2.0	-	0.3	-	-	-	-	0.1	-	89	98	63	99	100			
No.	99	2.0	-	0.3	-	-	-	-	-	0.1	87	98	61	97	100			
No.	100	2.0	-	0.3	-	-	0.1	-	-	-	90	98	60	97	99			
No.	101	2.0	-	0.3	-	-	0.3	-	-	-	90	98	60	95	100			
No.	102	2.0	-	0.3	-	-	0.1	-	-	-	87	97	58	95	99			
No.	103	2.0	-	0.3	-	-	-	-	0.1	-	88	96	60	57	60			
No.	104	2.0	-	0.3	-	-	-	-	-	0.1	87	96	60	59	60			
No.	105	2.0	-	-	-	-	0.3	-	0.1	-	-	90	99	59	97	100		
No.	106	2.0	-	-	-	-	0.3	-	0.3	-	-	91	99	61	99	100		
No.	107	2.0	-	-	-	-	0.3	-	0.1	-	-	92	98	60	59	60		
No.	108	1.0	2.0	-	-	-	0.3	-	-	0.1	-	90	98	60	57	58		
No.	109	1.0	2.0	-	-	-	0.3	-	-	0.1	-	92	97	60	57	58		
No.	110	-	3.0	-	-	-	0.3	-	0.3	-	-	85	97	60	55	53		
No.	111	-	3.0	-	-	-	0.3	-	0.3	-	-	69	96	60	56	52		
4th	No. 112	2.0	-	0.3	-	-	-	-	-	-	-	92	94	50	88	98		
Comp.	No. 113	2.0	-	-	0.3	-	-	-	-	-	-	92	96	100	47	88		
Ex.	No. 114	2.0	-	-	-	0.3	-	-	-	-	-	88	96	100	50	90		
	No. 115	2.0	-	-	-	-	0.3	-	-	-	-	69	97	100	38	91		

Examination for Purifying Performance

Each of the present catalysts and the comparative catalysts was disposed in an exhaust line of an actual vehicle equipped with a lean burn engine. The lean burn engine had a displacement of 1.6 liters. The vehicle  
5 was driven in the urban area running mode, for instance, it was alternately driven in the 10-mode for a certain period of time and then in the 15-mode for another certain period of time, thereby examining the present and comparative catalysts for the conversion of CO, HC and NO<sub>x</sub>. The results of the evaluation were summarized in the columns designated at "Initial Conversion" in Table 6.

After the aforementioned evaluation, each of the present catalysts and the comparative catalysts was subjected to a bench test on durability which utilized the same type of engine as above. Namely, each of them was disposed in an exhaust line of the engine, and then the engine was run for 100 hours while adjusting the temperature of the exhaust gas introduced into them at 650 °C. After this bench test was over, each of them was again disposed in the exhaust line of the actual vehicle. The vehicle was driven in the same manner as described above, thereby examining the present and comparative catalysts for the conversion of CO, HC and NO<sub>x</sub>. The results of the evaluation were summarized in the columns designated at "Conversion after Durability Test" in Table 6.

Evaluation

20 It is appreciated from Table 6 that the present catalysts with an alkaline-earth metal ingredient and a rare-earth element ingredient loaded were improved in terms of the NO<sub>x</sub> conversion after the durability test over the comparative catalysts with one and only alkaline-earth metal ingredient loaded.

Eighth Preferred Embodiments

25 A plurality of honeycomb supports with Pt or Pd loaded were prepared in the same manner as described in the "First Preferred Embodiments" section. Then, each of the supports was first immersed into an aqueous solution which contains barium acetate in a predetermined concentration, and it was dried thereafter. Moreover, four aqueous solutions containing one of lithium nitrate, lanthanum nitrate, cerium nitrate and zirconium oxy-nitrate in predetermined concentrations were prepared in this order. Each of the supports was further immersed into the four aqueous solutions in the order of the preparation of the aqueous solutions, and it was dried thereafter repeatedly. Each of the five aqueous solutions was prepared by mixing the solutes with water so as to load the five ingredients in loading amounts set forth in Table 7 below. Each of the supports was then blown to blow away the water droplets in excess. After drying, each of the supports was burned at 600 °C for 35 1 hour, thereby completing each of the present catalysts designated at No. 116 through No. 121 in Table 7.

Fifth Comparative Examples

40 Fifth Comparative Examples, e.g., comparative catalysts designated at No. 122 through No. 126 in Table 7 below, were prepared in the same manner as described in the "Eighth Preferred Embodiments" section except that either one of the five ingredients was not loaded thereon.

45

50

55

TABLE 7

Catalyst Ingredient (gram/liter)	Loading Amount, Ingredient (mole/liter)						Initial Conversion (%)			Conversion after Durability Test (%)		
	Pt	Pd	Li	Zr	Ba	Ca	NO <sub>x</sub>	CO	CO	NO <sub>x</sub>	HC	CO
8th Pref. Embodi- ments	No. 116 No. 117 No. 118 No. 119 No. 120 No. 121	2.0 - 2.0 - 2.0 -	0.2 0.2 0.1 0.05 0.2 0.2	0.1 0.1 0.05 0.05 0.1 0.1	0.5 0.5 0.3 0.3 0.5 0.5	0.2 0.2 0.1 0.1 0.2 0.2	0.5 0.5 0.1 0.1 0.2 0.2	91 88 92 92 91 91	93 94 93 92 92 92	71 98 98 97 95 96	95 93 95 95 95 90	99 98 98 98 99 91
5th Comp. Ex.	No. 122 No. 123 No. 124 No. 125 No. 126	2.0 2.0 2.0 2.0 2.0	- 0.2 0.2 0.2 0.2	0.1 0.5 - 0.1 0.1	0.5 0.5 0.2 0.5 0.5	0.2 0.2 0.2 0.5 0.2	0.5 0.5 0.5 0.5 0.2	93 92 73 91 85	91 92 93 93 94	45 49 35 52 53	93 91 91 90 91	99 99 99 99 98

Examination for Purifying Performance

Each of the present catalysts and the comparative catalysts was disposed in an exhaust line of an actual vehicle equipped with a lean burn engine. The lean burn engine had a displacement of 1.6 liters. The vehicle was driven in the urban area running mode, for instance, it was alternately driven in the 10-mode for a certain period of time and then in the 15-mode for another certain period of time, thereby examining the present and comparative catalysts for the conversion of CO, HC and NO<sub>x</sub>. The results of the evaluation were summarized in the columns designated at "Initial Conversion" in Table 7.

After the aforementioned evaluation, each of the present catalysts and the comparative catalysts was subjected to a bench test on durability which utilized the same type of engine as above. Namely, each of them was disposed in an exhaust line of the engine, and then the engine was run for 100 hours while adjusting the temperature of the exhaust gas introduced into them at 650 °C. After this bench test was over, each of them 5 was again disposed in the exhaust line of the actual vehicle. The vehicle was driven in the same manner as described above, thereby examining the present and comparative catalysts for the conversion of CO, HC and NO<sub>x</sub>. The results of the evaluation were summarized in the columns designated at "Conversion after Durability Test" in Table 7.

10 **Evaluation**

It is appreciated from Table 7 that the present catalysts with all of the five ingredients loaded were improved in terms of the NO<sub>x</sub> conversion after the durability test over the comparative catalysts lacking either one of the five ingredients.

15 Having now fully-described the present invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the present invention as set forth herein including the appended claims.

Disclosed are a catalyst and a process for purifying exhaust gases. The catalyst includes a porous support, Pt and/or Pd loaded on the porous support, and at least two ingredients loaded thereon and capable of reacting 20 with NO<sub>x</sub> and SO<sub>2</sub> contained in the exhaust gases to form nitrates and composite sulfates. Since the resulting composite sulfates are likely to decompose at low temperatures in the oxygen-lean atmospheres (i.e., in the fuel-rich atmospheres), the catalyst can absorb more NO<sub>x</sub> thereon. As a result, the catalyst can purify more NO<sub>x</sub>. Further, a second ingredient selected from the group consisting of transition elements can substitute for one of the two co-catalysts. Moreover, the catalyst is superb in the NO<sub>x</sub> purifying performance even after being 25 subjected to a harsh durability test. In the process, the catalyst is brought into contact with oxygen-rich exhaust gases, whose oxygen concentrations are the stoichiometric point or more required for oxidizing the components to be oxidized therein.

30 **Claims**

1. A catalyst for purifying exhaust gases, comprising:
  - a porous support; and
  - 35 at least one catalyst ingredient selected from the group consisting of Pt and Pd, and loaded on said porous support;
  - said catalyst is characterized in that:
    - at least two ingredients selected from the group consisting of rare-earth elements including La is further loaded on said porous support.
2. A catalyst for purifying exhaust gases, comprising:
  - a porous support; and
  - 40 at least one catalyst ingredient selected from the group consisting of Pt and Pd, and loaded on said porous support;
  - said catalyst is characterized in that:
    - at least one first ingredient selected from the group consisting of rare-earth elements including La is further loaded on said porous support; and
    - 45 at least one second ingredient selected from the group consisting of Fe, Ni, Co and Mn is further loaded on said porous support.
3. A catalyst for purifying exhaust gases, comprising:
  - a porous support; and
  - 50 at least one catalyst ingredient selected from the group consisting of Pt and Pd, and loaded on said porous support;
  - said catalyst is characterized in that:
    - at least two ingredients selected from the group consisting of alkali metals is further loaded on said porous support.
4. A catalyst for purifying exhaust gases, comprising:

a porous support; and  
at least one catalyst ingredient selected from the group consisting of Pt and Pd, and loaded on said porous support;  
said catalyst is characterized in that:  
5 at least one first ingredient selected from the group consisting of alkali metals is further loaded on said porous support; and  
at least one second ingredient selected from the group consisting of rare-earth elements including La is further loaded on said porous support.

10 5. A catalyst for purifying exhaust gases, comprising:  
a porous support; and  
at least one catalyst ingredient selected from the group consisting of Pt and Pd, and loaded on said porous support;  
said catalyst is characterized in that:  
15 at least one first ingredient selected from the group consisting of alkali metals is further loaded on said porous support; and  
at least one second ingredient selected from the group consisting of Fe, Ni, Co and Mn is further loaded on said porous support.

20 6. A catalyst for purifying exhaust gases, comprising:  
a porous support; and  
at least one catalyst ingredient selected from the group consisting of Pt and Pd, and loaded on said porous support; said catalyst is characterized in that:  
25 at least two ingredients selected from the group consisting of alkaline-earth metals are further loaded on said porous support.

25 7. A catalyst for purifying exhaust gases, comprising:  
a porous support; and  
at least one catalyst ingredient selected from the group consisting of Pt and Pd, and loaded on said porous support;  
30 said catalyst is characterized in that:  
at least one first ingredient selected from the group consisting of alkaline-earth metals is further loaded on said porous support; and  
at least one second ingredient selected from the group consisting of rare-earth elements including La is further loaded on said porous support.  
35

35 8. A catalyst for purifying exhaust gases, comprising:  
a porous support; and  
at least one catalyst ingredient selected from the group consisting of Pt and Pd, and loaded on said porous support;  
40 said catalyst is characterized in that:  
Ba, Li, La, Ce and Zr are further loaded on said porous support.

40 9. A process for simultaneously purifying carbon monoxide, hydrocarbons and nitrogen oxides in exhaust gases in oxygen-rich atmospheres, thereby purifying the exhaust gases, said process comprising the step of:  
45 bringing oxygen-rich exhaust gases, whose oxygen concentrations are the stoichiometric point or more required for oxidizing the components to be oxidized therein, into contact with a catalyst:  
said catalyst, comprising:  
a porous support; and  
50 at least one catalyst ingredient selected from the group consisting of Pt and Pd, and loaded on said porous support;  
said process is characterized in that:  
said catalyst further comprises:  
55 at least two ingredients selected from the group consisting of rare-earth elements including La, and loaded on said porous support.

55 10. A process for simultaneously purifying carbon monoxide, hydrocarbons and nitrogen oxides in exhaust gases in oxygen-rich atmospheres, thereby purifying the exhaust gases, said process comprising the step

of:

bringing oxygen-rich exhaust gases, whose oxygen concentrations are the stoichiometric point or more required for oxidizing the components to be oxidized therein, into contact with a catalyst:

said catalyst, comprising:

5 a porous support; and

at least one catalyst ingredient selected from the group consisting of Pt and Pd, and loaded on said porous support;

said process is characterized in that:

said catalyst further comprises:

10 at least one first ingredient selected from the group consisting of rare-earth elements including La, and loaded on said porous support; and

at least one second ingredient selected from the group consisting of Fe, Ni, Co and Mn, and loaded on said porous support.

15 11. A process for simultaneously purifying carbon monoxide, hydrocarbons and nitrogen oxides in exhaust gases in oxygen-rich atmospheres, thereby purifying the exhaust gases, said process comprising the step of:

bringing oxygen-rich exhaust gases, whose oxygen concentrations are the stoichiometric point or more required for oxidizing the components to be oxidized therein, into contact with a catalyst:

20 said catalyst, comprising:

a porous support; and

at least one catalyst ingredient selected from the group consisting of Pt and Pd, and loaded on said porous support;

said process is characterized in that:

said catalyst further comprises:

25 at least two ingredients selected from the group consisting of alkali metals, and loaded on said porous support.

30 12. A process for simultaneously purifying carbon monoxide, hydrocarbons and nitrogen oxides in exhaust gases in oxygen-rich atmospheres, thereby purifying the exhaust gases, said process comprising the step of:

bringing oxygen-rich exhaust gases, whose oxygen concentrations are the stoichiometric point or more required for oxidizing the components to be oxidized therein, into contact with a catalyst:

said catalyst, comprising:

35 a porous support; and

at least one catalyst ingredient selected from the group consisting of Pt and Pd, and loaded on said porous support;

said process is characterized in that:

said catalyst further comprises:

40 at least one first ingredient selected from the group consisting of alkali metals, and loaded on said porous support; and

at least one second ingredient selected from the group consisting of rare-earth elements including La, and loaded on said porous support.

45 13. A process for simultaneously purifying carbon monoxide, hydrocarbons and nitrogen oxides in exhaust gases in oxygen-rich atmospheres, thereby purifying the exhaust gases, said process comprising the step of:

bringing oxygen-rich exhaust gases, whose oxygen concentrations are the stoichiometric point or more required for oxidizing the components to be oxidized therein, into contact with a catalyst:

said catalyst, comprising:

50 a porous support; and

at least one catalyst ingredient selected from the group consisting of Pt and Pd, and loaded on said porous support;

said process is characterized in that:

said catalyst further comprises:

55 at least one first ingredient selected from the group consisting of alkali metals, and loaded on said porous support; and

at least one second ingredient selected from the group consisting of Fe, Ni, Co and Mn, and

loaded on said porous support.

14. A process for simultaneously purifying carbon monoxide, hydrocarbons and nitrogen oxides in exhaust gases in oxygen-rich atmospheres, thereby purifying the exhaust gases, said process comprising the step of:

5 bringing oxygen-rich exhaust gases, whose oxygen concentrations are the stoichiometric point or more required for oxidizing the components to be oxidized therein, into contact with a catalyst:

said catalyst, comprising:

a porous support; and

10 at least one catalyst ingredient selected from the group consisting of Pt and Pd, and loaded on said porous support;

said process is characterized in that:

said catalyst further comprises:

15 at least two ingredients selected from the group consisting of alkaline-earth metals, and loaded on said porous support.

14. A process for simultaneously purifying carbon monoxide, hydrocarbons and nitrogen oxides in exhaust gases in oxygen-rich atmospheres, thereby purifying the exhaust gases, said process comprising the step of:

20 bringing oxygen-rich exhaust gases, whose oxygen concentrations are the stoichiometric point or more required for oxidizing the components to be oxidized therein, into contact with a catalyst:

said catalyst, comprising:

a porous support;

25 at least one catalyst ingredient selected from the group consisting of Pt and Pd, and loaded on said porous support;

said process is characterized in that:

said catalyst further comprises:

30 at least one first ingredient selected from the group consisting of alkaline-earth metals, and loaded on said porous support; and

35 at least one second ingredient selected from the group consisting of rare-earth elements including La, and loaded on said porous support.

16. A process for simultaneously purifying carbon monoxide, hydrocarbons and nitrogen oxides in exhaust gases in oxygen-rich atmospheres, thereby purifying the exhaust gases, said process comprising the step of:

35 bringing oxygen-rich exhaust gases, whose oxygen concentrations are the stoichiometric point or more required for oxidizing the components to be oxidized therein, into contact with a catalyst:

said catalyst, comprising:

a porous support; and

40 at least one catalyst ingredient selected from the group consisting of Pt and Pd, and loaded on said porous support;

said process is characterized in that:

said catalyst further comprises:

Ba, Li, La, Ce and Zr loaded on said porous support.

45

50

55



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



⑪ Publication number : 0 613 714 A3

⑫

## EUROPEAN PATENT APPLICATION

⑬ Application number : 94100258.0

⑮ Int. CL<sup>5</sup> : B01D 53/36

⑭ Date of filing : 10.01.94

⑯ Priority : 11.01.93 JP 2491/93  
20.06.93 JP 206684/93  
24.09.93 JP 238461/93

⑰ Date of publication of application :  
07.09.94 Bulletin 94/36

⑱ Designated Contracting States :  
DE FR GB

⑲ Data of deferred publication of search report :  
05.10.94 Bulletin 94/40

⑳ Applicant : TOYOTA JIDOSHA KABUSHIKI KAISHA  
1, Toyota-cho  
Toyota-shi  
Aichi-ken (JP)

㉑ Applicant : KABUSHIKI KAISHA TOYOTA CHUO  
KENKYUSHO  
41-1, Aza Yokomichi  
Oaza Nagakute  
Nagakute-cho  
Aichi-gun Aichi-ken, 450-11 (JP)

㉒ Applicant : CATALER INDUSTRIAL CO., LTD.  
7800, Chihama,  
Daito-cho  
Ogase-gun, Shizuoka-ken (JP)

㉓ Inventor : Miyoshi, Naoto  
c/o Toyota Jidosa Kabushiki Kaisha,  
1, Toyota-cho  
Toyota-shi, Aichi-ken (JP)  
Inventor : Matsumoto, Shinichi  
c/o Toyota Jidosa Kabushiki Kaisha,  
1, Toyota-cho  
Toyota-shi, Aichi-ken (JP)  
Inventor : Tanizawa, Tsuneyuki  
c/o Toyota Jidosa Kabushiki Kaisha,  
1, Toyota-cho  
Toyota-shi, Aichi-ken (JP)  
Inventor : Iguchi, Satoshi  
c/o Toyota Jidosa Kabushiki Kaisha,  
1, Toyota-cho  
Toyota-shi, Aichi-ken (JP)

Inventor : Tanaka, Toshiaki  
c/o Toyota Jidosa Kabushiki Kaisha,  
1, Toyota-cho  
Toyota-shi, Aichi-ken (JP)  
Inventor : Takashima, Shinichi  
c/o Toyota Jidosa Kabushiki Kaisha,  
1, Toyota-cho  
Toyota-shi, Aichi-ken (JP)  
Inventor : Kanazawa, Takaaki  
c/o Toyota Jidosa Kabushiki Kaisha,  
1, Toyota-cho  
Toyota-shi, Aichi-ken (JP)  
Inventor : Hayashi, Takahiro  
c/o Toyota Jidosa Kabushiki Kaisha,  
1, Toyota-cho  
Toyota-shi, Aichi-ken (JP)  
Inventor : Saito, Motohisa, c/o K.K. Toyota Chuo  
Kenkyusho  
41-1, Aza Yokomichi,  
Oaza Nagakute,  
Nagakute-cho  
Aichi-gun, Aichi-ken (JP)  
Inventor : Dohmae, Kazuhiko, c/o K.K. Toyota Chuo  
Kenkyusho  
41-1, Aza Yokomichi,  
Oaza Nagakute,  
Nagakute-cho  
Aichi-gun, Aichi-ken (JP)  
Inventor : Yamazaki, Kiyoshi, c/o K.K. Toyota Chuo  
Kenkyusho  
41-1, Aza Yokomichi,  
Oaza Nagakute,  
Nagakute-cho  
Aichi-gun, Aichi-ken (JP)  
Inventor : Suzuki, Tadashi, c/o K.K. Toyota Chuo  
Kenkyusho  
41-1, Aza Yokomichi,  
Oaza Nagakute,  
Nagakute-cho  
Aichi-gun, Aichi-ken (JP)  
Inventor : Kasahara, Koichi  
c/o Cataler Industrial Co., Ltd.,  
7800, Chihama  
Daito-cho, Ogase-gun, Shizuoka-ken (JP)  
Inventor : Tabuchi, Syuji  
c/o Cataler Industrial Co., Ltd.,  
7800, Chihama  
Daito-cho, Ogase-gun, Shizuoka-ken (JP)

㉔ Representative : Bühlung, Gerhard, Dipl.-Chem. et al  
Patentanwaltsbüro  
Tiedtke-Bühlung-Klinne & Partner  
Bavariastr. 4  
D-80036 München (DE)

㉕ Catalyst and process for purifying exhaust gases.

㉖ A catalyst for purifying exhaust gases includes a porous support, at least one catalyst ingredient selected from Pt and Pd, and additional ingredients including (1) at least two rare-earth elements including La, (2) at least one rare-earth element including La and at least one transition element selected from Fe, Ni, Co and Mn, (3) at least two alkali metals, (4) at least one alkali metal and at least one rare-earth element including La, (5) at least one alkali metal and at least one transition element selected from Fe, Ni, Co and Mn, (6) at least two alkaline-earth metals, (7) at least one alkaline-earth metal and at least one rare-earth

element including La, or (8) Ba, Li, La, Ce and Zr. A process for purifying an exhaust gas, by contacting the catalyst with an exhaust gas, is also provided.

EP 0 613 714 A3



DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
P, X	EP-A-0 532 024 (SAKAI CHEMICAL IND. CO. LTD ET AL.) 17 March 1993 * claims 1-9 *	4,7,8, 12,15,16
P, X	EP-A-0 525 677 (DAIHATSU MOTOR CO. LTD. ET AL.) 3 February 1993 * claims 1-10 *	1,2,7,9, 10,15
X	EP-A-0 488 250 (TOYOTA JIDOSHA KK) * page 3, line 13 - line 43; claims 1-3 *	1,9
X	EP-A-0 441 173 (DEGUSSA AG)  * claim 1 *	1,2,4, 7-10,12, 15,16
X	EP-A-0 170 841 (W R GRACE & CO.)  * claims 1-21 *	1,2,4,9, 10,12
X	DE-A-37 43 626 (TOYOTA JIDOSHA KK ET AL.) * page 4, line 14 - line 17; claims 1-6 *	1,2,9,10
X	DE-A-37 26 580 (TOYOTA JIDOSHA KK) * claims 1-6 *	1,7,9,15
X	US-A-4 528 279 (TOYOTA JIDOSHA KOGYO KK ET AL.) * claims 1,2 *	1,9
X	US-A-4 497 783 (AMERICAN CYANAMID CO.) * abstract * * column 1, line 50 - line 58 *	3,11
X	EP-A-0 441 173 (DEGUSSA AG) * claim 1 *	5,13
		-/-
The present search report has been drawn up for all claims		
Place of search	Date of completion of the search	Examiner
THE HAGUE	1 August 1994	Eijkenboom, A
CATEGORY OF CITED DOCUMENTS		
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		
T : theory or principle underlying the invention E : earlier patent document, but published no, or after the filing date D : document cited in the application L : document cited in the other related		
A : member of the same patent family, corresponding document		



European Patent  
Office

### CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.
- Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claims:
- No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

### LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions, namely:

See sheet -B-



All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.



Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid,

namely claims:



None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims,

namely claims:



DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.CLS)		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim			
X	DE-A-40 08 371 (RIKEN KK) * page 2, line 63 - page 3, line 1 * * page 4, line 9 - line 15 * * page 4, line 36 - line 41 * -----	5,13			
X	EP-A-0 439 010 (NGK SPARK PLUG CO. LTD.) * page 3, line 43 - page 5, line 18 * * page 7, line 10 - line 23 * -----	6,14			
X	US-A-3 931 050 (NIPPON SOKEN INC. ET AL.) * claims 1,2 * -----	6,14			
			TECHNICAL FIELDS SEARCHED (Int.CLS)		
The present search report has been drawn up for all claims					
Place of search	Date of completion of the search	Inventor			
THE HAGUE	1 August 1994	Eijkenboom, A			
CATEGORY OF CITED DOCUMENTS					
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document					
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document					

**LACK OF UNITY OF INVENTION**

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims 1,2,4,7-10,12,15,16 : Cat.= Pt, Pd + RE +  
(RE or AM or AEM or Fe, Ni, Co,  
Mn or) or (Ba, Li, Zr)
2. Claims 3,5,11,13 : Cat. = Pt, Pd + AM + (AM or  
Fe, Ni, Co, Mn)
3. Claims 6,14 : Cat. = Pt, Pd + AEM + AEM

**See annex**

EP94100256

## LACK OF UNITY

**First invention:** A catalyst for purifying exhaust gases, comprising: a porous support and at least one catalyst ingredient from the group of Pt and Pd, said catalyst is characterized by:

one first ingredient from the group of rare-earth elements; and

Claim 1,9 one second ingredient from the group of rare-earth elements; or  
 Claim 2,10 Fe, Ni, Co, Mn; or  
 Claim 4,12 alkali metals; or  
 Claim 7,15 alkaline earth metal; or

Claim 8,16 said catalyst is characterized in that Ba, Li, La, Ce and Zr are further loaded on said porous support.

**Second invention:** A catalyst for purifying exhaust gases, comprising: a porous support and at least one catalyst ingredient from the group of Pt and Pd, said catalyst is characterized by:

one first ingredient from the group of alkali metals; and

Claim 3,11 one second ingredient from the group of alkali metals; or  
 Claim 5,13 Fe, Ni, Co, Mn.

**Third invention:** A catalyst for purifying exhaust gases, comprising: a porous support and at least one catalyst ingredient from the group of Pt and Pd, said catalyst is characterized by:

Claim 6,14 at least two ingredients from the group of alkaline earth metals.

\*\*\*\*\*

The claims 1,2,4,7-10,12,15,16 relating to the first invention contain a common technical feature (a catalyst containing one ingredient of the rare earth elements and one other ingredient) whilst the claims of the second and third invention do not have this characteristic.

Therefor the claims 3,5,6,11,13,14 are not searched without an additional payment of fees.